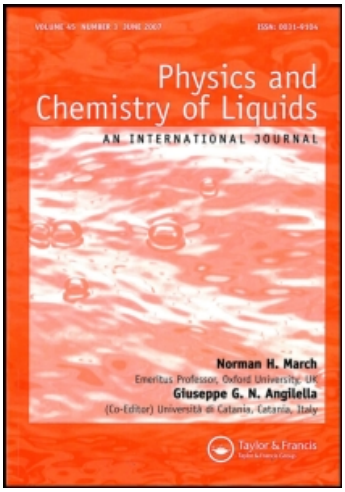

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Excess Volumes of *N, N*-Dimethyl Formamide and *N, N*-Dimethyl Acetamide with Aliphatic Esters at Room Temperature

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Excess Volumes of *N,N*-Dimethyl Formamide and *N,N*-Dimethyl Acetamide with Aliphatic Esters at Room Temperature

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Excess volumes for binary liquid mixtures of *N,N*-dimethylformamide and *N,N*-dimethylacetamide with ethylacetate, *n*-propylacetate *n*-butylacetate, iso-propylacetate and iso-amylacetate have been measured at 303.15 K. Excess volumes are negative in all the systems over the entire range of composition. The results have been discussed in terms of specific interactions between like and unlike molecules and the difference in size and shape of the component molecules.

KEY WORDS: Esters, chain length, dipolar association.

INTRODUCTION

In continuation of our study on excess thermodynamic properties of binary liquid mixtures containing amides as one of the component,[1] here we have reported excess volumes of *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) with (normal and branched esters) ethylacetate, *N*-propylacetate, *N*-butylacetate, iso-propylacetate and iso-amylacetate at 303.15 K. The influence of chain length and chain branching on excess volumes have been examined.

EXPERIMENTAL

Excess volumes were determined directly using a batch dilatometer technique described earlier[2] and the values were accurate to ± 0.003

Table 1 Boiling points and densities of the pure components at 303.15 K.

Component	Boiling point, K		Density, g cm^{-3}	
	Present work	Literature	Present work	Literature
DMF	425.85	426.00	0.94110	0.94120
DMA	439.00	439.10	0.93198	0.93230
Ethyl Acetate	350.00	350.11	0.88844	0.88847
n-Propyl Acetate	374.10	374.55	0.87616	0.87716
n-Butyl Acetate	399.10	399.12	0.87088	0.87129
Iso-propyl Acetate	361.00	361.20	0.86630	0.86640[a]
Iso-amyl Acetate	414.95	415.00	0.86675	0.86680[a]

[a] At 298.15 K.

$cm^3\ mol^{-1}$. All the chemicals were analytical grade commercial products. *N*,*N*-dimethylformamide (BDH) was purified by the methods described earlier.[1] *N*,*N*-dimethylacetamide was kept overnight over calcium hydride and fractionally distilled. The middle fraction of the distillate was collected. Ethylacetate (BDH), *N*-propylacetate (Sisco), iso-propylacetate (sisco) and iso-amylacetate (SD's) were dehydrated over potassium carbonate for two days, filtered and fractionally distilled. The middle fractions of the esters were redistilled with a fractionating column over phosphorous pentoxide. *N*-butylacetate (SD's) was kept over anhydrous magnesium sulphate for one day and fractionally distilled. The purity of the compounds was ascertained by comparing the values of density and boiling point with literature values[3,4] experimental and literature values are given in Table 1.

Table 2 Mole fraction x_1, Excess volume V^E and ΔV^E [a] at 303.15 K.

x_1	V^E	ΔV^E	x_1	V^E	ΔV^E
	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$		$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$
		DMF + Ethyl acetate			
0.1053	−0.1300	−0.001	0.5160	−0.3750	0.001
0.2139	−0.2440	−0.001	0.6178	−0.3490	−0.002
0.3135	−0.3200	0.001	0.7011	−0.3000	−0.001
0.4062	−0.3620	0.002	0.8459	−0.1690	0.001
		DMF + *n*-Propyl acetate			
0.1318	−0.1290	0.001	0.5343	−0.2870	0.001
0.2757	−0.2230	−0.001	0.7039	−0.2550	0.004
0.3191	−0.2450	−0.002	0.7939	−0.2100	0.003
0.4741	−0.2900	−0.005	0.9127	−0.1140	−0.001

Table 2 (*contd.*)

		DMF + *n*-Butyl acetate			
0.1565	−0.0930	−0.001	0.5071	−0.1840	0.003
0.2820	−0.1400	0.001	0.5408	−0.1920	−0.002
0.4043	−0.1720	−0.001	−0.6654	−0.1900	−0.003
0. 4801	−0.1820	0.002	0.7283	−0.1750	0.001
			0.8505	−0.1260	0.001
		DMF + Iso-propylacetate			
0.1127	−0.1750	−0.001	0.5531	−0.5150	−0.005
0.2778	−0.3770	0.002	0.6838	−0.4550	0.001
0.3367	−0.4310	0.001	0.7267	−0.4200	−0.001
0.4662	−0.5010	0.001	0.7939	−0.3460	0.001
			0.8653	−0.2480	−0.001
		DMF + Iso-Amylacetate			
0.1380	−0.0780	−0.001	0.5212	−0.2250	−0.001
0.2364	−0.1250	0.003	0.5780	−0.2300	−0.001
0.3222	−0.1670	0.001	0.6257	−0.2300	−0.002
0.4094	−0.2000	−0.001	0.7512	−0.1950	0.002
			0.8852	−0.1170	−0.001
		DMA + Ethylacetate			
0.1351	−0.1700	−0.001	0.5424	−0.3580	0.001
0.2708	−0.2820	0.001	0.6408	−0.3400	−0.001
0.3874	−0.3370	0.001	0.7455	−0.2870	−0.001
0.4546	−0.3540	0.001	0.9184	−0.1200	0.001
		DMA + *n*-propylacetate			
0.1428	−0.1300	−0.001	0.5413	−0.3100	−0.002
0.2241	−0.1950	0.001	0.6382	−0.2860	−0.002
0.3298	−0.2600	0.002	0.7513	−0.2220	0.001
0.4373	−0.3000	0.001	0.8376	−0.1550	0.001
		DMA + *n*-Butylacetate			
0.1081	−0.0850	−0.001	0.5306	−0.1670	0.001
0.2046	−0.1300	0.002	0.6692	−0.1440	−0.001
0.3547	−0.1670	0.001	0.7481	−0.1200	−0.001
0.4489	−0.1750	−0.001	0.8302	−0.0870	0.001
		DMA + Iso-propyl Acetate			
0.1051	−0.1900	0.001	0.6040	−0.3980	0.002
0.1649	−0.2710	−0.001	0.7081	−0.3450	0.002
0.3028	−0.3850	−0.001	0.8406	−0.2270	0.004
0.4422	−0.4300	−0.005	0.9481	−0.0900	−0.001
		DMA + Iso-Amyl Acetate			
0.1349	−0.1090	−0.001	0.5373	−0.1900	0.002
0.2021	−0.1440	0.001	0.5556	−0.1900	−0.001
0.3831	−0.1930	−0.001	0.6567	−0.1720	−0.001
0.4942	−0.1950	0.001	0.7140	−0.1540	−0.001
			0.8714	−0.0850	0.001

[a] $\Delta V^E = V^E(\text{expt}) - V^E(\text{Eq. 1})$.

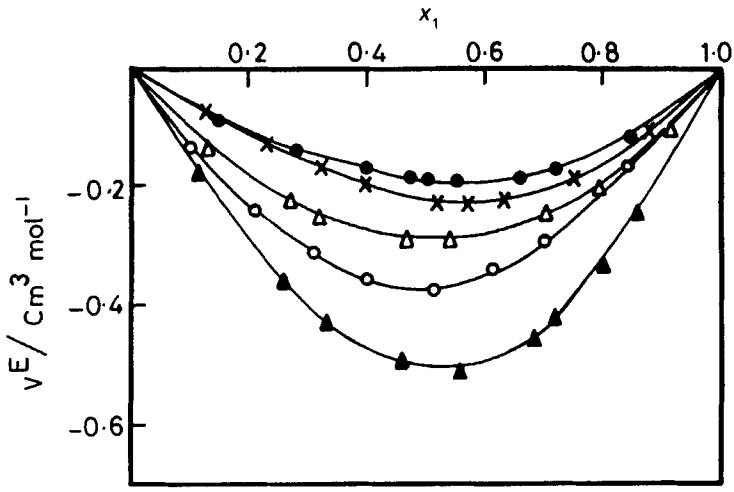

Figure 1 Excess volumes versus molefraction for DMF with Ethylacetate, ○; *n*-propylacetate, △; *n*-*b* Butylacetate, ●; Iso-propylacetate, ▲; Iso-amylacetate, ×.

RESULTS AND DISCUSSION

Excess volumes are given in Table 2 and also represented as a function of molefraction in Figures 1-2. The mole fraction dependence of excess volumes are represented by an empirical equation of the form.

$$V^E = x_1x_2[A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \quad (1)$$

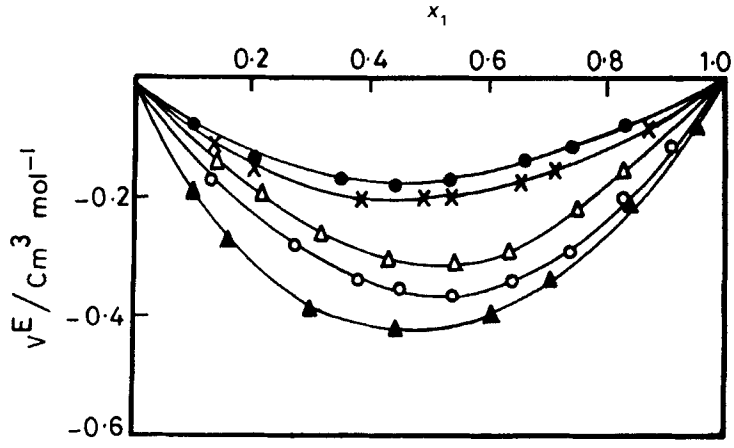

Figure 2 Excess volumes versus mole fraction for DMA with Ethylacetate, ○; *n*-propylacetate, △; *n*-butylacetate, ●; Iso-propylacetate, ▲; Iso-amylacetate, ×.

Table 3 Least square parameters and standard deviation for excess volumes ($cm^3\ mol^{-1}$).

System	a_0	a_1	a_2	$\sigma(V^E)$
DMF + Ethyl acetate	−1.5051	0.0789	0.3069	0.001
DMF + *n*-propyl acetate	−1.1469	−0.1554	−0.1952	0.003
DMF + *n*-Butyl acetate	−0.7453	−0.2101	−0.2117	0.002
DMF + Iso-propyl acetate	−2.0361	−0.2486	0.1705	0.002
DMF + Iso-Amyl acetate	−0.8860	−0.3372	−0.0048	0.002
DMA + Ethyl acetate	−1.4360	−0.0817	−0.1427	0.001
DMA + *n*-propyl acetate	−1.2369	−0.0514	0.2827	0.001
DMA + *n*-Butyl acetate	−0.6826	0.1561	−0.1067	0.001
DMA + Iso-propyl acetate	−1.6951	0.1757	−0.3270	0.003
DMA + Iso-Amyl acetate	−0.7803	0.1179	−0.1239	0.001

The values of the parameters A_0, A_1 and A_2 are obtained by the method of least squares and are given in Table 3 along with the standard deviation $\sigma(V^E)$.

The data presented in Table 2 and in figures reveal that the excess volumes are negative for all the systems over the whole range of composition. The algebraic values of V^E fall in the sequence: Iso-propyl acetate < ethylacetate < propylacetate < iso-amylacetate < butylacetate.

This order in V^E is the same with respect to the two amides. The results may be attributed to a resultant effect of two opposing factors, the mutual loss of dipolar association due to addition of second component and the presence of n–n interaction between unlike molecules. The negative values of V^E suggest that the latter effect may be dominant in all the mixtures. Further, a comparison of V^E results for normal esters with branched esters, in case of both the amides, reveal that the steric effect may contribute to negative excess volume. Finally, an examination of excess volumes for each ester with respect to two amides show that the results are slightly more negative in mixtures of *N*,*N*-dimethylformamide than in *N*,*N*-dimethylacetamide.

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